

Soy Oil Lutein Adsorption by Rice Hull Ash

Andrew Proctor* and Sevugan Palaniappan

Department of Food Science and Technology, Ohio State University, 2001 Fyffe Ct., Columbus, OH 43210-1096

Rice hull material was converted to an adsorbent of the soy oil pigment, lutein, by a combination of ashing and acid activation. Pigment was adsorbed from a 20% (v/v) soy oil/hexane miscella. The most effective ashing temperature was 500°C. Five percent acid activation significantly promoted adsorption of the ash, but greater acid activation did not increase adsorption capacity very much. In the system studied, the performance of activated ash was comparable to that of activated bleaching earth. Nonactivated ash also had an ability to bind lutein but was less effective than activated adsorbent. The absorbance spectrum of the residual lutein was not altered by rice hull ash, but was changed when exposed to bleaching clay.

The industrial refining of crude soy oil is important in producing a stable, bland, light-colored product acceptable to consumers. Bleaching is an important step in this process. The step involves heating the oil with natural or activated clays called "bleaching earths". Lutein, a carotenoid pigment, is adsorbed from the soy oil onto the surface of the earth, to produce a light-colored oil. Bleaching earth is composed mainly of montmorillonite, an aluminosilicate mineral. It has a natural ability to adsorb oil pigments which is greatly enhanced by acid activation (1).

There is interest in examining other materials as alternatives to conventional bleaching earths. For example, the Okija clay of Nigeria, where montmorillonite is unavailable, was found to be an effective alternative to traditional adsorbents (2). Alternatively, rice hulls are a biological source of silicate in the form of tridymite and cristobalite (3), and may have potential as a bleaching adsorbent. Rice hulls are burned by some cereal processors and the resulting ash consists of silicate minerals and a carbon residue (3). Modification of this material may provide an additional adsorbent for vegetable oil refining.

The purpose of this investigation was to study the potential of processed rice hull ash as an adsorbent of carotenoids from oil, using the extraction of lutein from soy oil in a model system. The effects of acid activation and dosage level of rice hull ash also were studied.

MATERIALS AND METHODS

Oil and solvents. Crude soy oil, obtained by commercial oil extraction, and hexane of high performance liquid chromatography (HPLC) grade were used. The crude oil was stored at 4°C. A 20% (v/v) soy oil/hexane miscella was prepared to evaluate adsorbent performance.

Ash production. Unless stated otherwise, the adsorbent was prepared as follows: Partially combusted rice hulls, hereafter referred to as "raw ash", were supplied by Riviana Foods (Houston, TX). Since the raw ash contained appreciable amounts of carbon, it was necessary to further combust the residue to obtain an exclusively

inorganic material. Samples were heated at 500°C for 10 hr in a muffle furnace. The pH of a 4% slurry of the residue in deionized water was measured and that residue was designated "alkaline ash". Forty grams of alkaline ash were mixed with 1 L of 20% (v/v) sulfuric acid for five hr at 20°C before being washed with an excess of deionized water, then filtered and dried in an oven at 100°C for four hr. The pH of a 4% suspension of this material in deionized water was measured and that residue was designated "acid ash".

Adsorbent dosage. Zero, 1, 2, 3, 4 and 5 g doses of alkaline ash, acid ash and official acid-activated bleaching clay (AOCS, Champaign, IL) were added to 100 ml of 20% (v/v) soy oil/hexane miscella. The miscellas were agitated with a magnetic stirrer for 15 min in a closed vessel at 20°C. The residual lutein concentration was measured by optical absorbance at 445 nm, according to the method of Proctor and Snyder (4). Five replicate readings were taken. Graphs were plotted of adsorbent dose against residual lutein and adsorbent dose against the amount of lutein adsorbed per g of adsorbent.

Ashing temperature. The adsorption experiment was repeated with 2 g of alkaline ash samples prepared by heating raw ash at either 500°C, 600°C, 700°C, 800°C, 900°C or 1000°C for 10 hr. The residual pigment concentration was then plotted against ashing temperature.

Acid activation. Alkaline ash samples, previously heated at 500°C, were acid activated with sulfuric acid concentrations of either 5, 10, or 20% sulfuric acid. The adsorption experiment was repeated using 2 g doses of each activated ash and the residual pigment concentration was plotted against percent acid activation.

Lutein absorbance spectrum. The absorbances of 100 ml miscellas between 350 nm and 550 nm were determined before and after mixing for 15 min with 2 g acid ash, 2 g alkaline ash and 2 g of acid activated bleaching clay.

RESULTS AND DISCUSSION

An approximate yield of 55% alkaline ash was obtained from raw ash. The pH of the alkaline ash was 8.65 and that of the acid ash was 6.62. The pH of the commercial bleaching clay was 3.40. These readings were the mean of triplicate determinations.

Preliminary studies demonstrated that raw ash had little affinity for pigment (data not shown). Figure 1 shows the residual lutein concentration of the miscella after mixing with various amounts of either alkaline ash, acid ash or bleaching earth. For each adsorbent, the greatest percent reduction in residual lutein concentration occurred between zero and one g of adsorbent added. However, larger doses did produce additional, but smaller, reductions in pigment concentration. Acid ash was comparable with the bleaching clay and was more effective than alkaline ash in reducing residual lutein concentration. This trend was also reflected in the relative pigment binding abilities of the adsorbents as seen in Figure 2. Acid ash and commercial bleaching clay had a

*To whom correspondence should be addressed.

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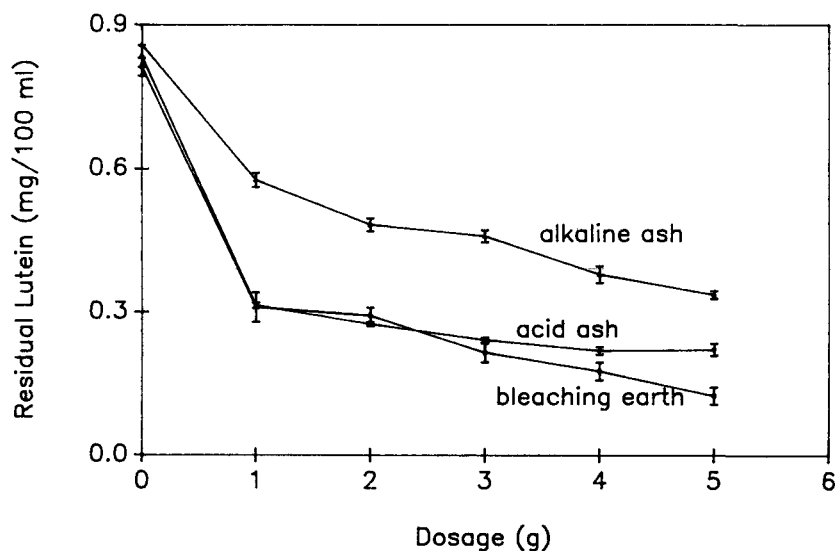


FIG. 1. Residual lutein concentrations were determined by incubating 100 ml of 20% (vol/vol) crude soy oil/hexane miscella for 15 min at 20°C with variable amounts of alkaline rice hull ash, acid rice hull ash and acid activated bleaching earth. Lutein concentrations were obtained by measuring absorbances 445 nm. Bars indicate standard error of the mean.

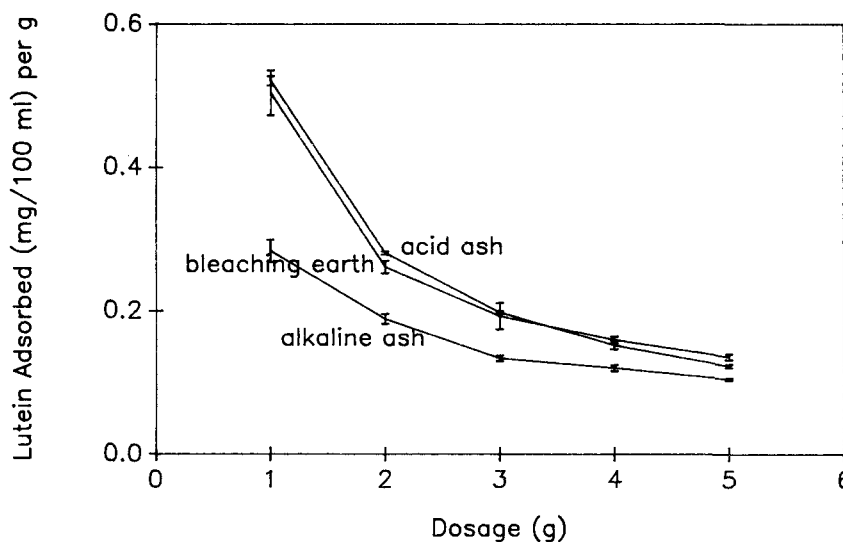


FIG. 2. Lutein adsorbed per gram of adsorbent was determined by incubating 100 ml of 20% (vol/vol) crude soy oil/hexane miscella for 15 min at 20°C with variable amounts of alkaline rice hull ash, acid rice hull ash and acid-activated bleaching earth. Lutein concentrations were obtained by measuring absorbance at 445 nm. Bars indicate standard error of the mean.

similar adsorptive capacity for pigment, and both were superior to that of alkaline ash. Smaller doses adsorbed more pigment per g in all cases. This has also been reported for silicic acid (4).

The data in Figures 1 and 2 suggest that the pigment binding abilities of acid ash and acid activated clay were similar. The increase in ash activity after acid activation parallels similar findings in conventional bleaching clays (5). Acid activation of montmorillonite opens up the crystal structure to produce a greater surface area available for adsorption. Performance is enhanced by displacement of aluminum and magnesium ions within the crystal (1). Cristobalite and tridymite consists of sheets of silica

tetrahedra with an open framework capable of accommodating cations. Aluminum is the most common cation and calcium and magnesium are also present (6). Activation of cristobalite and/or tridymite may be similar to montmorillonite. However, there are differences between the adsorbents. The acid ash had a much higher pH than the bleaching earth, and yet had a similar affinity for pigment. This may be due to differences in the adsorbent pore size or concentration of acid sites accessible to the pigment (7).

Heating raw ash above 500°C reduced the ability of the resulting alkaline ash to lower the lutein concentration of a miscella (Fig. 3). No further change in residual pigment

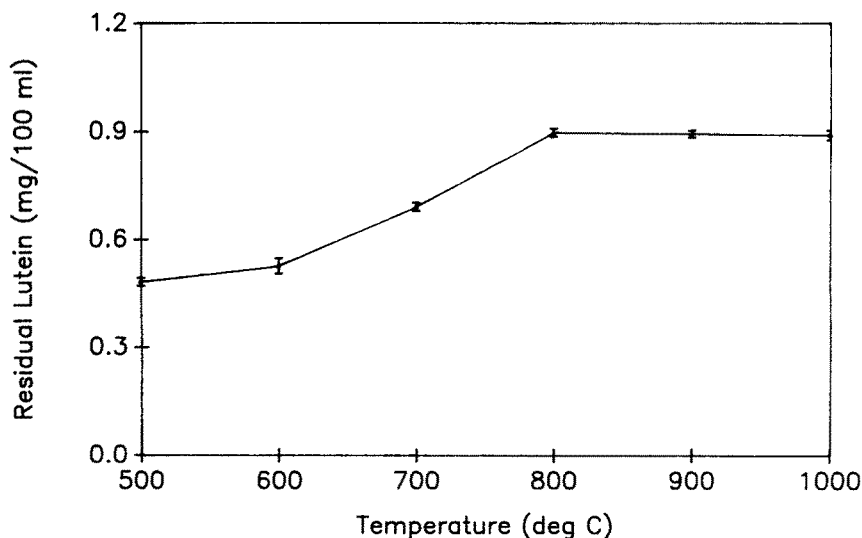


FIG. 3. Residual lutein concentrations were determined by incubating 100 ml of 20% (vol/vol) crude soy oil/hexane miscella for 15 min at 20°C with 2 g of alkaline rice hull ash, prepared by heating raw ash at different temperatures for 10 hr. Bars indicate standard error of the mean.

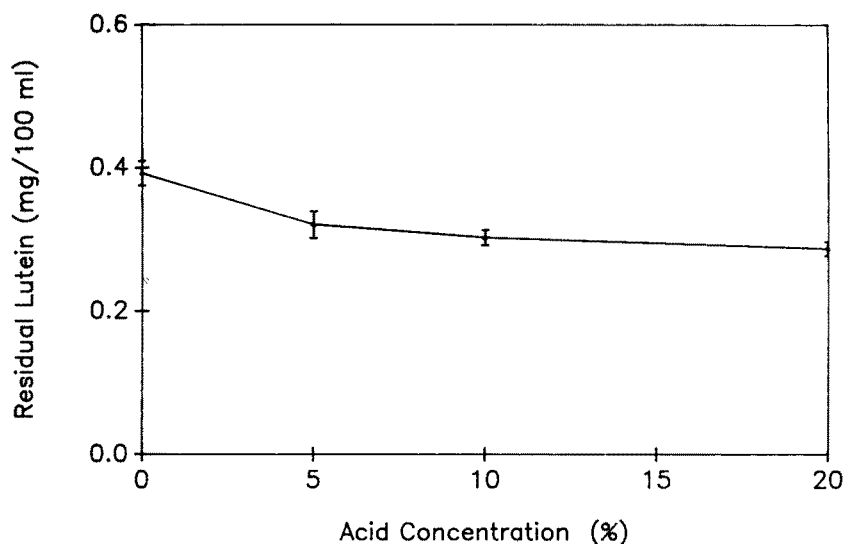


FIG. 4. Residual lutein concentrations were determined by incubating 100 ml of 20% (vol/vol) crude soy oil hexane miscella for 15 min at 20°C with 2 g of acid activated rice hull ash; acid activated with 0%, 5%, 10% and 20% sulfuric acid. Bars indicate standard error of the mean.

occurred when miscella was exposed to ash heated between 800-1000°C. This may be due to disruption of the crystal. Heat initiated the reduction in the adsorptive capacities of Tonsil and kaolin at 600°C (8). This was attributed to a breakdown of the crystal. Tridymite undergoes an endothermic reaction at 475°C which may affect crystal structure (6). In contrast to thermal activation, increasing the acid activation above 5% acid had no appreciable effect on residual pigment in the oil after bleaching (Fig. 4).

The data in Figure 5 show that there is no shift in the absorbance maxima of soy oil lutein at 421 nm, 445 nm and 474 nm when mixed with ash, but absorbance was diminished. After exposure to bleaching clay the lutein spectrum was removed. Khoo *et al.* (8) studied the

change in the absorbance spectrum of β -carotene in acetone when different adsorbents were added. Tonsil bleaching earth caused the removal of the β -carotene spectrum and an increase in absorbance between 330 and 360 nm. A similar observation was made in this study with bleaching earth. Khoo *et al.* (8) attributed this to oxygen independent catalysis of carotenoid breakdown on the surface of the adsorbent, in addition to chemisorption. Sarier and Guler (9) suggested that montmorillonite binds β -carotene from a benzene solution by chemisorption, and that the residual pigment is degraded by catalytic oxidation. In contrast, the consistency of the lutein spectrum, after adsorption by rice hull ash, is similar to findings obtained with silicic acid (8). This was indicative of physical adsorption and the absence of chemisorption.

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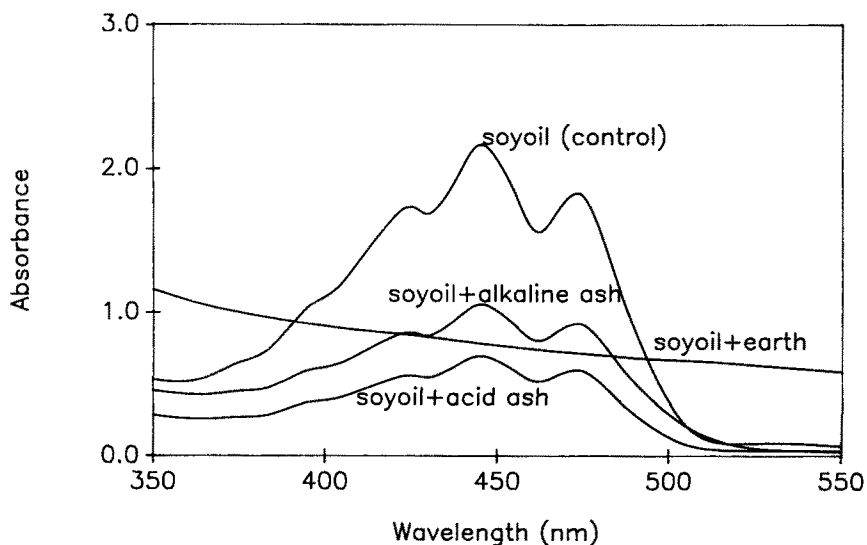


FIG. 5. Absorbance spectra were determined between 350 nm and 550 nm after incubating 100 ml of 20% (vol/vol) crude soy oil/hexane miscella for 15 min at 20°C with 2 g of alkaline rice hull ash, 2 g acid activated rice hull ash, and 2 g acid activated bleaching earth. A control of an untreated miscella is also presented.

However, in this study there was at least a slight greening of all the miscellas when exposed to adsorbents.

The results suggested that rice hulls can be made into an effective adsorbent of lutein and that acid activation promotes adsorption. Optimum conditions for processing rice hulls were an ashing temperature of 500°C and 5% acid activation.

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